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## (54) METHYLENE-BRIDGED POLYPHENYL POLYISOCYANATES

(71) We, E. I. DU PONT DE NEMOURS AND CO., a Corporation organised and existing under the laws of the State of Delaware, United States of America of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to new polyisocyanate compositions and their production and use.

It is well known to react a polyisocyanate with a polyfunctional, active hydrogen-containing compound such as a polyester, polyesteramide or polyether to produce rigid polyurethane materials. Foamed products are obtained by carrying out this reaction in the presence of a blowing agent such as carbon dioxide produced by the reaction of isocyanato groups with water, or a halogen-substituted alkane which is volatilized by heat generated in the polymerization reaction.

Polyisocyanates used to produce rigid foams should give foams of high thermal insulating power, low density and high compressive strength. In addition it is important that the polyisocyanate be of sufficiently low viscosity to allow ease of handling and mixing with other reactants, and should also be of low volatility, since the flame resistance of the resulting foam increases with decreasing volatility of the polyisocyanate.

Many isocyanate compositions are known which can be used to make rigid foams. U.S. Patent No. 3,316,286 discloses tolylene diisocyanate solutions of non-volatile polyisocyanate scutels, and U.S. Patent No. 2,683,730 and Canadian Patent No. 700,726 disclose methylene-bridged polyphenyl polyisocyanates, all of which can be used to make rigid foams. While some of these polyisocyanates and others

of a similar nature give foams having good physical properties, they are deficient in some respects. Foams prepared from polyisocyanates containing significant quantities of tolylene diisocyanate (TDI) frequently have poor flame resistance because of the high volatility of TDI. Foams prepared from known methylene-bridged polyphenyl polyisocyanate mixtures, though better than the TDI-based foams, are also somewhat deficient in flame resistance because of the high proportion of diisocyanatodiphenylmethane (MDI) in the polyisocyanate mixtures. The flame resistance of these foams can be improved by removing MDI from the isocyanate mixture by distillation, but this operation can adversely affect the quality of the isocyanates and cause an unacceptable increase in their viscosity because of the formation of polymeric isocyanate by-products, particularly when producing polyisocyanate compositions of low MDI content.

There is a need, therefore, for an isocyanate composition which will produce rigid foams of good physical properties and improved flame resistance, yet be of sufficiently low viscosity to be readily handled and mixed.

According to this invention a new polyisocyanate composition, useful in the preparation of rigid foams, is prepared by (1) reacting at least 2.5 moles of aniline with 1 mole of formaldehyde in the presence of a mineral acid, forming an intermediate methylene-bridged polyphenyl polyamide mixture, (2) removing methylenedianiline (MDA) from said intermediate polyamine mixture to leave a polyamine residue containing not more than 55% by weight of methylenedianiline, and (3) phosgenating this polyamine residue to give the corresponding polyisocyanate composition. Polyisocyanate compositions so prepared are inexpensive and are lower in viscosity at a given MDI content than methylene-bridged

polyphenyl polyisocyanate mixtures prepared by known methods.

The invention consists also in rigid foams made from the new polyisocyanate compositions, which are high in flame-resistance when the polyisocyanate composition is low in MDI content.

The polyisocyanate compositions of this invention are essentially mixtures of methylene-bridged polyphenyl polyisocyanates of the general formula



wherein  $n$  is at least 1. The polyisocyanate mixtures contain from about 0—55% diisocyanatodiphenylmethane and at least half the remaining portion consists of 2,4 - bis(p - isocyanatobenzyl)phenyl isocyanate. (Proportions are by weight except when otherwise stated). Other polyisocyanates present are tetra- (and higher) functional methylene-bridged polyphenyl polyisocyanates. The compositions may also contain a minor amount (10% or less) of complex condensation and phosgenation by-products having biuret, isocyanate dimer, isocyanurate and urea type structures.

The MDA and MDI contents of polyamine and polyisocyanate mixtures described herein are determined by quantitative fractional distillation at 1 mm. Hg pressure, with a final distillation temperature of 270°C. for polyamines and 240—250°C. for polyisocyanates. Under these conditions substantially all of the difunctional material is collected as distillate. The MDA and MDI contents are calculated as follows:

$$\% \text{ MDA or MDI} = \frac{\text{distillate, parts}}{\text{sample, parts}} \times 100$$

The intermediate polyamine mixture can be made in the conventional manner as disclosed for example in U.S. Patents Nos. 2,818,433, 2,974,168, 3,163,166 (without solvent treating step) and 3,367,969. Aniline and formaldehyde are reacted in the presence of a mineral acid preferably hydrochloric acid, though other mineral acids, such as sulphuric acid, can be used. While the exact amount of acid used is not particularly critical, the practical range is between about 0.4 and 2 moles, preferably 0.8—1.0 moles, per equivalent of amine. The mineral acid will, of course, form salts with the amines present and it is to be understood that the term "mineral acid" is meant to include salts of the acid with the amine. Also the aniline which reacts with the formaldehyde can be in the form of the free amine or a salt of the mineral acid.

After the reaction is complete, the reaction mass is neutralised with an alkaline material such as sodium carbonate or sodium hydroxide. The resulting aqueous and organic phases

are separated, and residual water, unreacted aniline, and the desired amount of methylenedianiline are distilled off under reduced pressure, leaving the polyamine residue, which is then phosgenated by known methods such as are described in the patents cited above. The final polyamine residue can also be prepared by removing larger amounts of MDA from the intermediate polyamine mixture, and then adding distilled or undistilled MDA to bring the MDA content up to the desired level. The MDA prepared by the above process is predominantly 4,4' - methylene - dianiline, but minor amounts of the 2,4' - isomer may also be present.

In order that the polyisocyanate compositions may have the desirable properties disclosed herein, it is important that the mole ratio of aniline to formaldehyde in the initial reaction be at least 2.5:1. The preferred ratios are from about 2.8:1 to 3.0:1, partly for economic reasons, and partly because the polyisocyanate compositions then obtained have a particularly desirable combination of low viscosity and volatility. In one preferred method for carrying out the aniline-formaldehyde reaction, described in column 1, lines 39—50 of U.S. Patent No. 2,818,433, higher mole ratios of aniline to formaldehyde, even up to 10:1, can be used to prepare polyamine mixtures, but the use of mole ratios above about 3:1 increases the expense of the operation because of the cost of hydrochloric acid and neutralising agent as well as the initial cost of aniline and expense of its recovery, and provides no significant benefit in improved properties of the polyisocyanate compositions obtained.

The intermediate polyamide mixtures contain at least about 70% MDA, but enough is distilled off to give a final polyamine residue containing from about 0.55%. The lower the MDA content, the lower will be the volatility and the higher will be the viscosity of the polyisocyanates prepared from the polyamine residues. It has been discovered, however, that even though the isocyanate compositions of this invention contain little or no MDI, their viscosity is low enough for them to be easily handled and mixed with polyols, polyamines, etc. to prepare foams. The higher the ratio of aniline to formaldehyde employed in the initial reaction, the lower will be the viscosity of the final polyisocyanate composition at a given MDI content. Polyisocyanate compositions having particularly desirable combinations of viscosity, volatility and functionality are prepared when the initial aniline to formaldehyde ratio is from about 2.8:1 to 3.0:1, and the MDA content of the polyamine residue is about 0—25%.

The polyisocyanate compositions of this invention have a significant economic advantage over known methylene-bridged polyphenyl polyisocyanates in that they can be prepared

from polyamine residues which have heretofore been discarded. Thus, in the manufacture of MDA, a compound having substantial commercial use, by condensing aniline and formaldehyde, substantial quantities of tri-, tetra- and higher functional amine are prepared. MDA is distilled off from these higher boiling polyfunctional amines and, before the present invention, the latter were discarded as useless by-products. The present invention utilizes these residues by phosgenating them to useful polyisocyanate compositions providing a readily available, inexpensive source for a major component used in the manufacture of polyurethane foams. The polyamine residues utilised in this invention cannot be prepared directly by condensation of aniline and formaldehyde as taught in the prior art, at any weight ratio of the two reactants.

As already stated, foams prepared from the preferred isocyanate compositions of the invention have greater flame resistance than those prepared from prior art methylene-bridged polyphenyl polyisocyanates of the same viscosity, because of their low MDI content.

For example, "PAPI" (Registered Trade Mark), a well-known commercial methylene-bridged polyphenyl polyisocyanate of Brookfield viscosity of about 250—400 centipoises at 25°C, contains about 45—50% MDI, whereas one polyisocyanate composition of this invention having a Brookfield viscosity of 300 centipoises at 30°C, has an MDI content of 24% (Example 3). Thus, polyisocyanate compositions of this invention have, at a given viscosity, a lower proportion of MDI than the methylene-bridged polyphenyl polyisocyanates of the prior art which

are prepared from polyamine mixtures obtained directly from the condensation of aniline and formaldehyde.

The rigid foams can be made conventionally by reacting the polyisocyanate compositions with polyalkylenether or polyester glycols or other polyols in the presence of an expanding agent, using either the pre-polymer or the one-shot technique. The new polyisocyanate compositions are particularly useful for preparing foams by the "one shot" technique. Methods for preparing rigid foams, and representative polyols and glycols which can be used, are disclosed in numerous references, e.g. Saunders and Frisch, "High Polymers", Vol. XVI, Polyurethanes: Chemistry and Technology, Interscience Publishers, New York, in Chapter 8 entitled "Rigid Foams"; U.S. Patent No. 3,194,773; and the following bulletins of the Elastomer Chemicals Dept., E. I. du Pont de Nemours & Co.: R. A. Stengard, "General Questions Often Asked About Rigid Urethane Foam", March 1, 1962, revised Sept. 1966, and E. Tufts and W. I. Touhey, "Moulding One-Shot Resilient Urethane Foam", Nov. 3, 1962. Foams prepared with the polyisocyanate compositions of this invention have good physical properties; e.g. their thermal insulating power, compressive strength, and dimensional stability are comparable to those of high quality foams prepared from prior art methylene-bridged polyphenyl polyisocyanates.

The invention is illustrated in the following Examples wherein parts and percentages are by weight unless otherwise indicated and the physical and chemical properties of isocyanates and foams are measured as follows:

Isocyanate content	ASTM D 1638—61 T
Compressive strength	ASTM D 1621—64
Thermal conductivity	
(K factor)	ASTM C 177—63
Dimensional stability	ASTM D 794—64 T
Friability	ASTM C 421—61
Density	ASTM D 1622—63

#### EXAMPLE 1

An intermediate polyamine mixture containing 85—86% MDA is prepared by reacting 3 moles of aniline with 1 mole of formaldehyde in the presence of 2.64—2.88 moles hydrochloric acid. Methylenedianiline is removed from the product by distillation at 5—10 mm. Hg. to a final temperature of the residue of 260—300°C., leaving a residue containing 3—6% MDA. A solution of 303 g. of the distillation residue in 1500 ml. of o-dichlorobenzene is slowly charged to a vigorously agitated mixture of 566 g. of phosgene and 1600 ml. of o-dichlorobenzene while maintaining the temperature at 0—10°C. by

external cooling. After addition of the amine is complete, phosgene is continuously introduced at a rate of about 75 g./hr. The temperature is slowly raised to 160° C. over 4 hours, and is then maintained at 160—165°C. for 90 minutes. The reaction mixture is then swept by a vigorous stream of nitrogen at 150°C. for one hour to remove unreacted phosgene and by-product hydrochloric acid. The solvent is distilled off at a pressure of 20 mm. Hg, and the last traces of low-boiling material are removed at 170°C. and 1 mm. Hg. The product comprises 384 g. of liquid polyisocyanate material having the following properties:

	Isocyanate content, %	30.9	Physical properties of the foam are shown below.	
	Number average molecular weight (cryoscopic method in benzene)	451	Density lb./cu. ft.	2.35
5	Brookfield viscosity at 30°C., cps. (determined with RVT model, spindle No. 2, 5 RPM)	3250	K factor, BTU/hr/ft <sup>2</sup> /°F/in.	0.121
	Functionality (Calc.)	3.32	K factor after ageing 4 weeks at room temp.	0.145
			Friability, % loss (ASTM Method C-421)	11.8
10	On prolonged standing at room temperature partial crystallisation of the polyisocyanate takes place. Upon heating to 50—60°C. the composition turns completely liquid, and it remains so for several days even on standing at room temperature.		Compressive strength	
			Parallel to blow psi at yield point	38
15	Extraction of the polyisocyanate composition with hexane yields about 60% of the essentially pure 2,4 - bis(p - isocyanatobenzyl)-phenyl isocyanate.		% Deflection at yield point	7
	The liquid polyisocyanate composition is used in the preparation of rigid polyurethane foam as follows:		Perpendicular to blow psi at yield point	24
20	The isocyanate composition is mixed with a polyol using the following formulation:		% Deflection at yield	8
			Dimensional stability, linear, %	
			1 day at 100°C.	1
			1 day at -25°C.	-0.5
			7 days at 100°C.	2.5
			7 days at -26°C.	-5
				75
			EXAMPLE 2	
25	Condensation product of propylene oxide and methyl glucoside having a hydroxyl number of about 435 and a Brookfield viscosity of about 18,000 cps. at 25°C. (available from Olin Mathieson Chemical Corp. as "Poly G-435 DM")	100	An amine mixture containing 85—86% MDA and not more than 0.05% water and 0.1% aniline is prepared by reacting 3 moles of aniline with 1 mole of formaldehyde in the presence of hydrochloric acid.	80
30	Foam stabilising surfactant, a hydrolytically stable poly(oxyalkylene) poly(dimethylsiloxane) block copolymer (available commercially as DC-793 from the Dow Corning Corp.)	2	3407 grams of the crude product is partially distilled at a pressure of 1 mm. Hg and a pot temperature of 200—220°C. The fraction collected within 7 hours consists of methylenedianiline (2282 g., 66.8%, b.p. 190°—205°C.). The distillation residue amounts to 1121 g. (32.9% of the total charge), which contains about 55% methylenedianiline and 45% higher condensation products.	85
35	N,N,N',N'-Tetramethyl - 1,3 - butanediamine	2	The distillation residue is dissolved in 4000 ml. of dry o - dichlorobenzene, and the solution is added to a solution of 1460 g. (14.75 moles) of phosgene in 5000 ml. of o - dichlorobenzene at 0° to 60°C. with vigorous agitation. After addition is complete, continuous introduction of phosgene is begun at a rate of about 195 g./hr. The temperature is slowly raised to 165°C. (over a period of about 4 hours) and is maintained at 160°—165°C. for two hours. Phosgene addition is then discontinued, and the reaction mixture is swept by a vigorous stream of nitrogen at 150°C. for 1 hour to remove excess phosgene and by-product hydrochloric acid. The solvent is distilled off at a pressure of 20 mm. Hg, and the last traces of low boilers are removed at 170°C. and 1 mm. Hg. The yield of polyisocyanate material is 1412 g.	90
40	Triethylamine	1	The polyisocyanate composition has the following properties:	95
	Trichlorofluoromethane	35		
	Polyisocyanate composition	114		
45	Mixing time is about 10 seconds. The mixture is poured into a mould and allowed to foam.			100
50	The resulting foam is self-extinguishing when tested by ASTM Method D 1692-59T. A foam of similar density prepared using 110 parts of PAPI as the isocyanate composition has a rating of "burning", using the same test.			105
55	(PAPI is a commercial methylene-bridged polyphenyl polyisocyanate of NCO content 30.4—31.5%, Brookfield viscosity 250—400 cps. at 25°C. and MDI content 45—50%.)			110

	Isocyanate content, (determined by titration with dibutylamine)	31.1%	Isocyanate content	31.15%	55
5	Number average molecular weight (cryoscopic method in benzene)	350	Number average molecular weight (isopiestic method in benzene)	385	
	Functionality (Calcd.)	2.6	Functionality (Calc.)	2.86	
	Content in distillable MDI	55%	Content of Distillable MDI	23.8	60
	Brookfield viscosity at 30°C.,	155 cps	Brookfield viscosity at 30°C. (determined with RVT, model, spindle No. 2, 100 RPM)	300 cps.	
10	A rigid foam is prepared by mixing this polyisocyanate composition with a polyol using the following formulation:				
		Parts	Canadian Patent No. 760,026 (Example 10, p. 58) teaches that a methylene-bridged polyphenyl polyisocyanate having a substantially higher MDI content (35—37%) has a Brookfield viscosity of 1500 centipoises at 25°C., and that a polyisocyanate composition having an MDI content comparable to that of the polyisocyanate of this Example (about 24%) is too viscous to be suitably handled for foam production (page 23).		
15	Condensation product of propylene oxide and sorbitol of hydroxyl number 440—460 and Brookfield viscosity at 25°C. 11,000—15,000 centistokes (available from Atlas Chemical Industries as "Atpol" 2571)	85			70
20	N,N,N',N' - Tetraakis(2 - hydroxypropyl) - ethylene - diamine	15	WHAT WE CLAIM IS:—		75
25	Dimethylpolysiloxane - polyalkylene oxide block copolymer (Hydrolytically stable liquid of specific gravity 1.04 and a viscosity of 1200—1500 centistokes available from General Electric Co. as SF-1066)	2	1. A process for the production of a methylene-bridged polyphenyl polyisocyanate composition, which comprises (1) reacting at least 2.5 moles of aniline with 1 mole of formaldehyde in the presence of a mineral acid, (2) removing methylene-dianiline from the resulting polyamine mixture to leave a polyamine residue containing not more than 55% by weight of methylenedianiline, and (3) phosgenating the polyamine residue to give a polyisocyanate composition.		80
30	N,N,N',N' - Tetramethyl - 1,3 - butanediamine	0.3	2. Process according to claim 1, wherein the distillation of the methylenedianiline is continued until the residue contains 0—25% by weight thereof.		85
	1,4 - Diazabicyclo[2.2.2]octane	0.5	3. Process according to claim 1 or 2, wherein the mole ratio of aniline to formaldehyde is from 2.8:1 to 3.0:1.		90
	Trichlorofluoromethane	39	4. A process for the production of a polyisocyanate composition according to claim 1 substantially as hereinbefore described.		95
	Polyisocyanate composition	124	5. A polyisocyanate composition obtained by a process claimed in any one of claims 1 to 4.		
35	The ingredients are mixed for about 28 seconds with a high speed laboratory mixer and the blend is poured into a suitable mould and allowed to foam. The foam time, that is the time required for the foam to reach maximum height from the start of mixing, is 165 seconds. The resulting foam has the following physical properties:				
	Density, lb./cu. ft.	2.15	6. A process for preparing a polyurethane rigid foam, which comprises reacting a polyisocyanate composition claimed in claim 5 with a polyol in the presence of a blowing agent.		100
	K-Factor	0.117	7. Rigid foams obtained by the process of claim 6.		105
45	Yield point, psi	41.5			
	Deflection at yield, %	9.3			

#### EXAMPLE 3

- 50 A polyisocyanate composition is prepared by blending a sample of the amine distillation residue of Example 1 with 20% by weight of MDA and phosgenating the amine mixture by the procedure described in Example 1. The resulting liquid polyisocyanate material has the following properties:

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